

# ELECTROLYTE FOR ELECTROCHEMICAL DEVICE

## BACKGROUND OF THE INVENTION

5 The present invention relates to an electrolyte, an ion conductor including the electrolyte, and electrochemical devices including the electrolyte, such as lithium cells, lithium ion cells, electrical double-layer capacitors.

10 Accompanying the evolution of portable equipment in recent years, there has been active development of electrochemical devices utilizing electrochemical phenomena, such as cells for use as their power supplies and capacitors. In addition, electrochromic devices (ECD), in which a color change occurs due to an electrochemical reaction, are examples of electrochemical devices for uses other than power supplies.

15 These electrochemical devices are typically composed of a pair of electrodes and an ion conductor filled between them. The ion conductor contains a salt (AB) as an electrolyte, which is dissolved in a solvent, polymer or mixture thereof such that the salt is dissociated into cations ( $A^+$ ) and anions ( $B^-$ ), resulting in ionic conduction. In order to obtain the required level of ion  
20 conductivity for the device, it is necessary to dissolve a sufficient amount of this electrolyte in solvent or polymer. In actuality, there are many cases in which a solvent other than water is used, such as organic solvents and polymers. Electrolytes having sufficient solubility in such organic solvents and polymers are  
25 presently limited to only a few types. For example, electrolytes having sufficient solubility for use in lithium cells are only  $LiClO_4$ ,  $LiPF_6$ ,  $LiBF_4$ ,  $LiAsF_6$ ,  $LiN(SO_2CF_3)_2$ ,  $LiN(SO_2C_2F_5)_2$ ,  $LiN(SO_2CF_3)(SO_2C_4F_9)$  and  $LiCF_3SO_3$ . Although the cation type of the electrolyte is frequently limited by the device as is the case  
30 with the lithium ion of lithium cells, any anion can be used for the electrolyte provided it satisfies the condition of having high solubility.

Amidst the considerable diversity of the application range of these devices, efforts are made to seek out the optimum electrolyte for each application. Under the present circumstances, however, optimization efforts have reached their limit due to the limited types of available anions. In addition, existing electrolytes have various problems, thereby creating the need for an electrolyte having a novel anion portion. More specifically, since  $\text{ClO}_4$  ion of  $\text{LiClO}_4$  is explosive and  $\text{AsF}_6$  ion of  $\text{LiAsF}_6$  is toxic, they cannot be used for reasons of safety. Even the only practical electrolyte of  $\text{LiPF}_6$  has problems including heat resistance and hydrolysis resistance. Although electrolytes of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  and  $\text{LiCF}_3\text{SO}_3$  are stable and high in ionic conductivity, they corrode the aluminum collector inside the cell when a potential is applied. Therefore, their use presents difficulties.

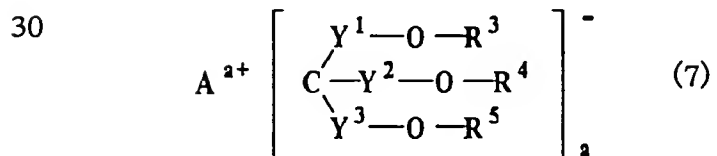
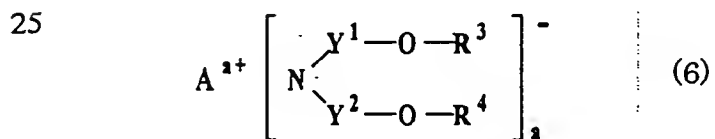
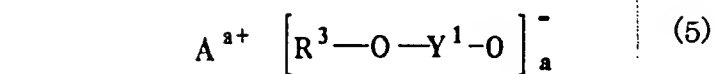
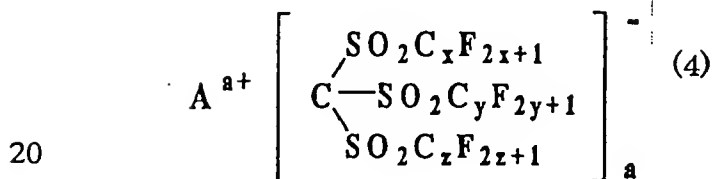
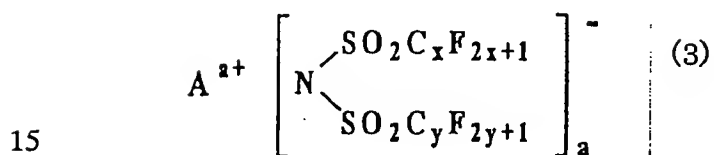
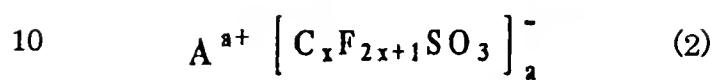
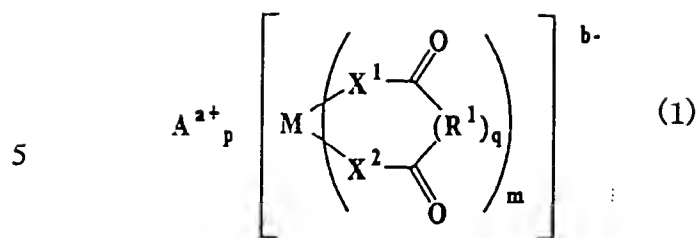
#### SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a useful novel electrolyte, a novel ion conductor containing the electrolyte, and a novel electrochemical device containing the ion conductor.

According to the present invention, there is provided an electrolyte for an electrochemical device. This electrolyte comprises:

a first compound that is an ionic metal complex represented by the general formula (1); and

at least one compound selected from the group consisting of second to fourth compounds respectively represented by the general formulas (2) to (4), fifth to ninth compounds respectively represented by the general formulas  $\text{A}^+(\text{PF}_6^-)_a$ ,  $\text{A}^+(\text{ClO}_4^-)_a$ ,  $\text{A}^+(\text{BF}_4^-)_a$ ,  $\text{A}^+(\text{AsF}_6^-)_a$ , and  $\text{A}^+(\text{SbF}_6^-)_a$ , and tenth to twelfth compounds respectively represented by the general formulas (5) to (7),



wherein M is a transition metal selected from the group consisting of elements of groups 3-11 of the periodic table, or an element selected from the group consisting of elements of groups 12-15 of the periodic table;

- 5         $A^{a+}$  represents a metal ion, hydrogen ion or onium ion;  
          a represents a number from 1 to 3; b represents a number from 1 to 3; p is b/a; m represents a number from 1 to 4; q is 0 or 1;

- $R^1$  represents a  $C_1$ - $C_{10}$  alkylene group,  $C_1$ - $C_{10}$  halogenated alkylene group,  $C_4$ - $C_{20}$  arylene group or  $C_4$ - $C_{20}$  halogenated  
 10        arylene group, these alkylene and arylene groups of said  $R^1$  optionally having substituents and hetero atoms, one of said  $R^1$  being optionally bonded with another of said  $R^1$ ;

         each of  $X^1$  and  $X^2$  independently represents O, S or  $NR^2$ ;

- $R^2$  represents a hydrogen,  $C_1$ - $C_{10}$  alkyl group,  $C_1$ - $C_{10}$   
 15        halogenated alkyl group,  $C_4$ - $C_{20}$  aryl group or  $C_4$ - $C_{20}$  halogenated aryl group, these alkyl and aryl groups of said  $R^2$  optionally having substituents and hetero atoms, at least two of said  $R^2$  being optionally bonded together to form a ring;

- each of x, y and z independently represents a number from 1  
 20        to 8

         each of  $Y^1$ ,  $Y^2$  and  $Y^3$  independently represents a  $SO_2$  group or CO group; and

- each of  $R^3$ ,  $R^4$  and  $R^5$  independently represents an  
          electron-attractive organic substituent optionally having a  
 25        substituent or a hetero atom, at least two of said  $R^3$ ,  $R^4$  and  $R^5$  being optionally bonded together to form a ring, at least one of said  $R^3$ ,  $R^4$  and  $R^5$  being optionally bonded with an adjacent molecule to form a polymer.

- According to the present invention, there is provided an ion  
 30        conductor for an electrochemical device. This ion conductor comprises the electrolyte; and a member selected from the group consisting of a nonaqueous solvent, a polymer and a mixture thereof, said member dissolving therein said electrolyte.

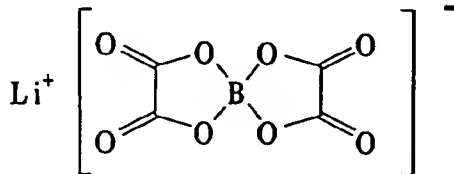
According to the present invention, there is provided an electrochemical device comprising (a) first and second electrodes; and (b) the ion conductor receiving therein said first and second electrodes.

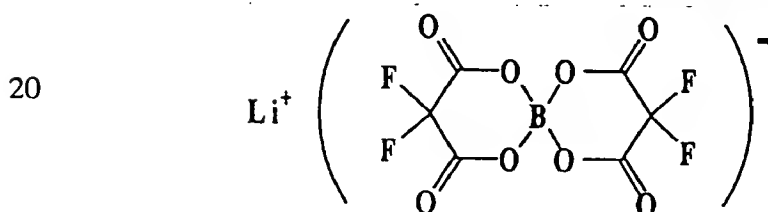
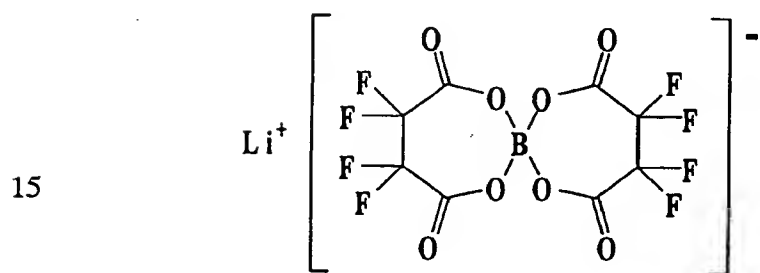
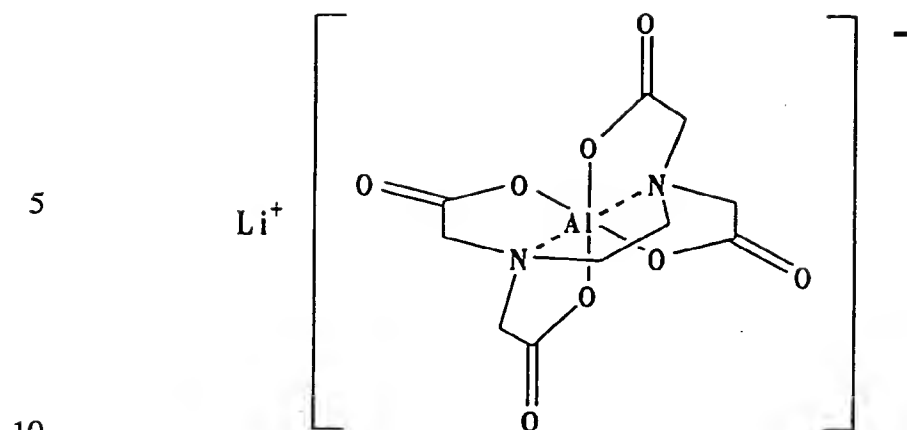
5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

An electrolyte according to the present invention is superior in cycle characteristics and shelf life as compared with conventional electrolytes. Thus, the electrolyte can advantageously be used for electrochemical devices such as  
10 lithium cell, lithium ion cell and electrical double-layer capacitor.

According to the invention, the alkyl groups, halogenated alkyl groups, aryl groups and halogenated aryl groups, which are contained in the ionic metal complex and the raw materials for synthesizing the same, may be branched and/or may have other  
15 functional groups such as hydroxyl groups and ether bonds.

The followings are specific four examples of the ionic metal complex represented by the general formula (1) of the present invention.





25 Here, although lithium ion is indicated as an example of  $A^{a+}$  of the general formula (1), examples of other cations that can be used other than lithium ion include sodium ion, potassium ion, magnesium ion, calcium ion, barium ion, cesium ion, silver ion, zinc ion, copper ion, cobalt ion, iron ion, nickel ion, manganese ion, titanium ion, lead ion, chromium ion, vanadium ion, ruthenium  
30 ion, yttrium ion, lanthanoid ion, actinoid ion, tetrabutylammonium ion, tetraethylammonium ion, tetramethylammonium ion, triethylmethylammonium ion, triethylammonium ion, pyridinium ion, imidazolium ion, hydrogen

ion, tetraethylphosphonium ion, tetramethylphosphonium ion, tetraphenylphosphonium ion, triphenylsulfonium ion, and triethylsulfonium ion. In the case of considering the application of the ionic metal complex for electrochemical devices and the like, 5 lithium ion, tetraalkylammonium ion and hydrogen ion are preferable. As shown in the general formula (1), the valency (valence) of the  $A^{a+}$  cation is preferably from 1 to 3. If the valency is larger than 3, the problem occurs in which it becomes difficult to dissolve the ionic metal complex in solvent due to the increase in 10 crystal lattice energy. Consequently, in the case of requiring solubility of the ionic metal complex, a valency of 1 is preferable. As shown in the general formula (1), the valency ( $b^-$ ) of the anion is similarly preferably from 1 to 3, and a valency of 1 is particularly preferable. The constant  $p$  expresses the ratio of the 15 valency of the anion to the valency of the cation, namely  $b/a$ .

In the general formula (1),  $M$  at the center of the ionic metal complex of the present invention is selected from elements of groups 3-15 of the periodic table. It is preferably Al, B, V, Ti, Si, Zr, Ge, Sn, Cu, Y, Zn, Ga, Nb, Ta, Bi, P, As, Sc, Hf or Sb, and more 20 preferably Al, B or P. Although it is possible to use various elements for the  $M$  other than these preferable examples, synthesis is relatively easy in the case of using Al, B, V, Ti, Si, Zr, Ge, Sn, Cu, Y, Zn, Ga, Nb, Ta, Bi, P, As, Sc, Hf or Sb. In addition to ease of synthesis, the ionic metal complex has excellent 25 properties in terms of low toxicity, stability and production cost in the case of using Al, B or P.

In the general formula (1), the organic or inorganic portion bonded to  $M$  is referred to as the ligand. As mentioned above,  $R^1$  in the general formula (1) represents a  $C_1$ - $C_{10}$  alkylene group, 30  $C_1$ - $C_{10}$  halogenated alkylene group,  $C_4$ - $C_{20}$  arylene group or  $C_4$ - $C_{20}$  halogenated arylene group. These alkylene and arylene groups optionally have substituents and hetero atoms. For example, hydrogen of these alkylene and arylene groups may be replaced

with halogen, an acyclic or cyclic alkyl group, aryl group, alkenyl group, alkoxy group, aryloxy group, sulfonyl group, amino group, cyano group, carbonyl group, acyl group, amide group or hydroxyl group. Furthermore, carbon of the alkylene and arylene groups  
 5 may be replaced with nitrogen, sulfur or oxygen. When the first compound has a plurality of  $R^1$  in the molecule, these  $R^1$  may be bonded together. In this case, the ligand may be in the form like that of ethylenediaminetetraacetic acid.

Each of  $X^1$  and  $X^2$  in the general formula (1) independently  
 10 represents O, S or  $NR^2$ , and is bonded to M through its hetero atom (O, S or N). Although the bonding of an atom other than O, S or N is not impossible, the synthesis becomes extremely bothersome. The ionic metal complex represented by the general formula (1) is characterized by these ligands forming a chelate  
 15 structure with M since there is bonding with M by  $X^1$  and  $X^2$  within the same ligand. As a result of this chelation, the heat resistance, chemical stability and hydrolysis resistance of the ionic metal complex are improved. Although constant q in this ligand is either 0 or 1, in the case of 0 in particular, since the chelate ring  
 20 becomes a five-member ring, chelating effects are demonstrated most prominently, making this preferable due to the resulting increase in stability.

In the general formula (1),  $R^2$  represents a hydrogen,  $C_1-C_{10}$  alkyl group,  $C_1-C_{10}$  halogenated alkyl group,  $C_4-C_{20}$  aryl group or  
 25  $C_4-C_{20}$  halogenated aryl group. These alkyl and aryl groups optionally have substituents and hetero atoms, and at least two of  $R^2$  are optionally bonded together to form a ring.

In the general formula (1), the value of the constant m relating to the number of the above-mentioned ligands depends on  
 30 the type of the central M. In fact, m is preferably from 1 to 4.

According to a first preferred embodiment of the invention, the electrolyte contains the ionic metal complex represented by the general formula (1) and another component that is at least one



compound selected from the above-mentioned second to fourth compounds represented by the general formulas (2), (3) and (4). Examples of these compounds are  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  and  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ . If the ionic metal complex is omitted in the first preferred embodiment, the following problem occurs. That is, the another component corrodes the aluminum collector inside the cell when a potential is applied. With this, the capacity is lowered by repeating the charge and discharge cycle. In contrast, according to the first preferred embodiment, the aluminum collector corrosion can unexpectedly be prevented by using a mixture of the ionic metal complex and the another component. The reason of this is not clear. It is, however, assumed that the ionic metal complex is slightly decomposed on the electrode surface and that a film of the ionic metal complex's ligand is formed on the aluminum surface, thereby preventing the aluminum collector corrosion.

According to a second preferred embodiment of the invention, the electrolyte contains the ionic metal complex represented by the general formula (1) and another component that is at least one compound selected from the above-mentioned fifth to ninth compounds respectively represented by the general formulas  $\text{A}^+(\text{PF}_6^-)_a$ ,  $\text{A}^+(\text{ClO}_4^-)_a$ ,  $\text{A}^+(\text{BF}_4^-)_a$ ,  $\text{A}^+(\text{AsF}_6^-)_a$ , and  $\text{A}^+(\text{SbF}_6^-)_a$  where  $\text{A}^+$  is preferably the same ion as that in the general formula (1). If the ionic metal complex is omitted in the second preferred embodiment, the following problem occurs. That is, the anion(s) tends to be pyrolyzed at a high temperature of  $60^\circ\text{C}$  or higher, thereby generating a Lewis acid(s). This Lewis acid decomposes the solvent and makes the electrochemical device inferior in performance and lifetime. Furthermore, the omission of the ionic metal complex causes hydrolysis of the anion(s) when the electrolyte is contaminated with a very small amount of water. This hydrolysis generates an acid(s) that makes the electrochemical device inferior in performance and lifetime. In

contrast, according to the second preferred embodiment, the above-mentioned pyrolysis and hydrolysis can unexpectedly be prevented by using a mixture of the ionic metal complex and the another component. The reason of this is not clear. It is, however, assumed that the properties of the solution as a whole change somehow to achieve this prevention by a certain interaction between the ionic metal complex and the another component.

According to a third preferred embodiment of the invention, the electrolyte contains the ionic metal complex represented by the general formula (1) and another component that is at least one compound selected from the above-mentioned tenth to twelfth compounds represented by the general formulas (5), (6) and (7). Examples of these compounds are  $\text{CF}_3\text{CH}_2\text{OSO}_3\text{Li}$ ,  $(\text{CF}_3)_2\text{CHOSO}_3\text{Li}$ ,  $(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{NLi}$ ,  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$ ,  $(\text{CF}_3\text{CH}_2\text{OSO}_2)((\text{CF}_3)_2\text{CHOSO}_2)\text{NLi}$ ,  $((\text{CF}_3)_3\text{COSO}_2)_2\text{NLi}$ , and  $((\text{CF}_3)_2\text{CHOSO}_2)_3\text{CLi}$ . Further examples are polymers and oligomers such as  $[\text{N}(\text{Li})\text{SO}_2\text{OCH}_2(\text{CF}_2)_4\text{CH}_2\text{OSO}_2]_n$  where  $n$  is a number of 2-1,000. If the ionic metal complex is omitted in the third preferred embodiment, the following problem occurs. That is, the another component corrodes the aluminum collector inside the cell when a potential is applied. With this, the capacity is lowered by repeating the charge and discharge cycle. In contrast, according to the third preferred embodiment, the aluminum collector corrosion can unexpectedly be prevented by using a mixture of the ionic metal complex and the another component. The reason of this is not clear. It is, however, assumed that the ionic metal complex is slightly decomposed on the electrode surface and that a film of the ionic metal complex's ligand is formed on the aluminum surface, thereby preventing the aluminum collector corrosion.

In the invention, the molar ratio of the ionic metal complex to the at least one compound is preferably 1:99 to 99:1 (or a range

from 5:95 to 95:5), more preferably 20:80 to 80:20 (or a range from 30:70 to 70:30), in view of improving the electrochemical device in cycle characteristics and shelf life. If this ratio is less than 1:99 (or 5:95), it may become insufficient to prevent the

5 above-mentioned aluminum corrosion and/or the above-mentioned pyrolysis and hydrolysis, thereby making the electrolyte inferior in cycle characteristics and shelf life. If the ratio is greater than 99:1 (or 95:5), advantages of adding the at least one compound to increase ionic conductivity and electrochemical stability may  
10 become insufficient.

In the case of preparing an electrochemical device of the present invention, its basic structural elements are ion conductor, negative electrode, positive electrode, collector, separator, container and the like.

15 A mixture of electrolyte and non-aqueous solvent or polymer is used as the ion conductor. If a non-aqueous solvent is used, the resulting ion conductor is typically referred to as an electrolytic solution, while if a polymer is used, it is typically referred to as a polymer solid electrolyte. Non-aqueous solvent may also be  
20 contained as plasticizer in polymer solid electrolytes.

There are no particular restrictions on the non-aqueous solvent provided it is an aprotic solvent that is able to dissolve an electrolyte of the present invention, and examples of this non-aqueous solvent that can be used include carbonates, esters,  
25 ethers, lactones, nitriles, amides and sulfones. In addition, the solvent can either be used alone or in the form of a mixture of two or more types of solvent. Specific examples of the solvent include propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, methylethyl carbonate, dimethoxyethane,  
30 acetonitrile, propionitrile, tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, nitromethane, N,N-dimethylformamide, dimethylsulfoxide, sulfolane and  $\gamma$ -butyrolactone.

In case that  $A^{a+}$  of the general formula (1) is lithium ion, the non-aqueous solvent of an electrolytic solution is preferably a mixture of a first aprotic solvent having a dielectric constant of 20 or greater and a second aprotic solvent having a dielectric constant of 10 or less. In fact, lithium salt has a low solubility in the second aprotic solvent (e.g., diethyl ether and dimethyl carbonate). Therefore, it may be difficult to obtain a sufficient ionic conductivity by using only the second aprotic solvent. In contrast, lithium salt has a high solubility in the first aprotic solvent. The resulting solution is, however, high in viscosity. Thus, it may be difficult to obtain a sufficient ionic conductivity by using only the first aprotic solvent, too. In contrast, it becomes possible to gain a suitable solubility and a suitable ionic mobility by using a mixture of the first and second aprotic solvents, thereby making it possible to obtain a sufficient ionic conductivity.

There are no particular restrictions on the polymer to be mixed with the electrolytes of the invention provided it is an aprotic polymer. Examples of such polymer include polymers having polyethylene oxide on their main chain or side chain, homopolymers or copolymers of polyvinylidene fluoride, methacrylate polymers and polyacrylonitrile. In the case of adding plasticizer to these polymers, the above-mentioned aprotic non-aqueous solvent can be used. The total concentration of the electrolytes of the present invention in these ion conductors is preferably 0.1 mol/dm<sup>3</sup> or more up to the saturated concentration, and more preferably from 0.5 mol/dm<sup>3</sup> to 1.5 mol/dm<sup>3</sup>. If the concentration is lower than 0.1 mol/dm<sup>3</sup>, ion conductivity may become too low.

There are no particular restrictions on the negative electrode material for preparing an electrochemical device. In the case of lithium cell, lithium metal (metallic lithium) or an alloy of lithium and another metal can be used. In the case of a lithium ion cell, it is possible to use an intercalation compound containing lithium

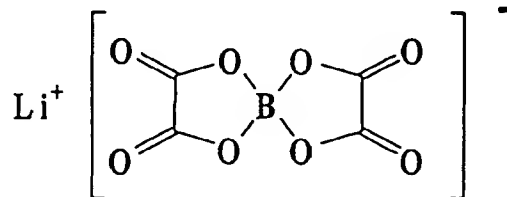
atoms in a matrix of another material, such as carbon, natural graphite or metal oxide. This carbon can be obtained by baking polymer, organic substance, pitch or the like. In the case of electrical double-layer capacitor, it is possible to use activated carbon, porous metal oxide, porous metal, conductive polymer and so forth.

There are no particular restrictions on the positive electrode material. In the case of lithium cell or lithium ion cell, lithium-containing oxides such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMnO}_2$  and  $\text{LiMn}_2\text{O}_4$ ; oxides such as  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$ ; sulfides such as  $\text{TiS}_2$  and  $\text{FeS}$ ; and electrically conductive polymers such as polyacetylene, polyparaphenylene, polyaniline or polypyrrole can be used. In the case of electrical double-layer capacitor, activated carbon, porous metal oxide, porous metal, electrically conductive polymer and so forth can be used.

The following nonlimitative examples are illustrative of the present invention. In fact, Examples 1-1 to 1-5 are illustrative of the above-mentioned first preferred embodiment of the invention, and Examples 2-1 to 2-4 are illustrative of the above-mentioned second preferred embodiment of the invention, and Examples 3-1 to 3-4 are illustrative of the above-mentioned third preferred embodiment of the invention.

#### EXAMPLE 1-1

A lithium borate derivative, represented by the following formula, and  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  were dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a lithium borate derivative concentration of 0.05 mol/liter and a  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  concentration of 0.95 mol/liter.



Then, ion conductivity of the electrolytic solution was measured with an alternating current bipolar-type cell. As a result, the ion conductivity was 7.3 mS/cm at 25°C.

5 A corrosion test of an aluminum collector was performed using the above-mentioned electrolytic solution. A beaker type cell was used for the test cell, using aluminum for the working electrode, and lithium metal (metallic lithium) for the counter electrode and reference electrode. When the working electrode was held at 5 V (Li/Li<sup>+</sup>), there was no flow of current whatsoever.  
10 Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

A charging and discharging test of an actual cell was conducted using the above-mentioned electrolytic solution. The  
15 test cell (half cell) was prepared in the manner described below. The positive electrode was prepared by mixing 5 parts by weight of polyvinylidene fluoride (PVDF) as a binder and 5 parts by weight of acetylene black as a conductor with 90 parts by weight of a LiCoO<sub>2</sub> powder followed by the addition of  
20 N,N-dimethylformamide to form a paste. This paste was applied to an aluminum foil and allowed to dry to obtain the test positive electrode. Lithium metal was used for the negative electrode. A glass fiber filter as a separator was impregnated with the electrolytic solution, thereby assembling the cell.

25 Next, a constant current charging and discharging test was conducted as described below. The current density was 0.35 mA/cm<sup>2</sup> for both charging and discharging, while charging was performed until 4.2 V and discharging until 3.0 V (vs. Li/Li<sup>+</sup>). As a result, the initial discharge capacity was 118 mAh/g (the positive  
30 electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 93% of the initial capacity.

#### EXAMPLE 1-2

A lithium borate derivative, represented by the same formula as that of Example 1-1, and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  were dissolved in a mixture of propylene carbonate (PC) and diethyl carbonate (DEC) (PC:DEC = 1:1 by volume) to prepare an electrolytic solution  
5 having a lithium borate derivative concentration of 0.10 mol/liter and a  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  concentration of 0.90 mol/liter. Then, ion conductivity of the electrolytic solution was measured with an alternating current bipolar-type cell. As a result, the ion conductivity was 8.9 mS/cm at 25°C.

10 A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V (Li/Li<sup>+</sup>), there was no flow of current whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes  
15 observed in comparison with that before testing.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 1-1. As a result, the initial discharge capacity was 115  
20 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 85% of the initial capacity.

#### EXAMPLE 1-3

25 A lithium borate derivative, represented by the same formula as that of Example 1-1, and  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  were dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a lithium borate derivative concentration of 0.05  
30 mol/liter and a  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  concentration of 0.95 mol/liter. Then, ion conductivity of the electrolytic solution was measured with an alternating current bipolar-type cell. As a result, the ion conductivity was 6.5 mS/cm at 25°C.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V (Li/Li<sup>+</sup>), there was no flow of current whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 1-1. As a result, the initial discharge capacity was 120 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 91% of the initial capacity.

#### EXAMPLE 1-4

A lithium borate derivative, represented by the same formula as that of Example 1-1, and LiN(SO<sub>2</sub>CF<sub>3</sub>)(SO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>) were dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a lithium borate derivative concentration of 0.95 mol/liter and a LiN(SO<sub>2</sub>CF<sub>3</sub>)(SO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>) concentration of 0.05 mol/liter. Then, ion conductivity of the electrolytic solution was measured with an alternating current bipolar-type cell. As a result, the ion conductivity was 6.9 mS/cm at 25°C.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V (Li/Li<sup>+</sup>), there was no flow of current whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and discharging test was conducted in the same manner as that of



Example 1-1. As a result, the initial discharge capacity was 120 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 94% of the initial capacity.

#### EXAMPLE 1-5

A solution was prepared by adding acetonitrile to 70 parts by weight of a polyethylene oxide (average molecular weight: 10,000). Then, 5 parts by weight of a lithium borate derivative, represented by the same formula as that of Example 1-1, and 25 parts by weight of  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  were added to the solution. The resulting mixture was cast on a glass, followed by drying to remove the acetonitrile. With this, a polymer solid electrolyte film was prepared.

A corrosion test of an aluminum collector was performed using a laminate including the solid electrolyte film interposed between an aluminum electrode (working electrode) and a lithium electrode. This laminate was prepared by press welding. When the working electrode was held at 5 V ( $\text{Li}/\text{Li}^+$ ), there was no flow of current whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, except in that the polymer solid electrolyte film was used in place of the electrolytic solution and the separator. Then, a constant current charging and discharging test was conducted at 70°C as described below. The current density was 0.1 mA/cm<sup>2</sup> for both charging and discharging, while charging was performed until 4.2 V and discharging until 3.0 V (vs.  $\text{Li}/\text{Li}^+$ ). As a result, the initial discharge capacity was 120 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 89% of the initial

capacity.

#### COMPARATIVE EXAMPLE 1-1

At first,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  was dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  concentration of 1.0 mol/liter.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li}/\text{Li}^+$ ), corrosion current was observed. Following testing, the surface of the working electrode was observed by SEM. With this, many pits were observed on its surface. It is assumed that these pits were caused by corrosion.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 1-1. As a result, the initial discharge capacity was 117 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 69% of the initial capacity.

#### COMPARATIVE EXAMPLE 1-2

At first,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  was dissolved in a mixture of propylene carbonate (PC) and diethyl carbonate (DEC) (PC:DEC = 1:1 by volume) to prepare an electrolytic solution having a  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  concentration of 1.0 mol/liter.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li}/\text{Li}^+$ ), corrosion current was observed. Following testing, the surface of the working electrode was observed by SEM. With this, many pits were observed on its surface. It is assumed that these pits were caused by corrosion.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and

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discharging test was conducted in the same manner as that of Example 1-1. As a result, the initial discharge capacity was 112 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 67% of the initial capacity.

### COMPARATIVE EXAMPLE 1-3

At first,  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  was dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  concentration of 1.0 mol/liter.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li}/\text{Li}^+$ ), corrosion current was observed. Following testing, the surface of the working electrode was observed by SEM. With this, many pits were observed on its surface. It is assumed that these pits were caused by corrosion.

The test cell (half cell) was prepared in the same manner as that of Example 1-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 1-1. As a result, the initial discharge capacity was 118 mAh/g (the positive electrode capacity). Although charging and discharging were repeated 100 times, results were obtained in which the capacity of the 100<sup>th</sup> cycle was 74% of the initial capacity.

### EXAMPLE 2-1

An electrolytic solution was prepared by the same manner as that of Example 1-1, except that  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$  was replaced with  $\text{LiPF}_6$ . This electrolytic solution had a lithium borate derivative concentration of 0.05 mol/liter and a  $\text{LiPF}_6$  concentration of 0.95 mol/liter.

A charging and discharging test of an actual cell was conducted using the above-mentioned electrolytic solution. The

test cell was prepared in the manner described below. The positive electrode of  $\text{LiCoO}_2$  was prepared by the same manner as that of Example 1-1. The negative electrode of natural graphite was prepared by mixing 10 parts by weight of polyvinylidene fluoride (PVDF) as a binder with 90 parts by weight of a natural graphite powder followed by the addition of N,N-dimethylformamide to form a slurry. This slurry was applied to an copper foil and allowed to dry at  $150^\circ\text{C}$  for 12 hr to obtain the test negative electrode. A polyethylene separator was impregnated with the electrolytic solution, thereby assembling the cell.

Next, a constant current charging and discharging test was conducted at  $70^\circ\text{C}$  under the following conditions. The current density was  $0.35 \text{ mA/cm}^2$  for both charging and discharging, while charging was performed until 4.2 V and discharging until 3.0 V (vs.  $\text{Li/Li}^+$ ). Although charging and discharging were repeated 500 times, results were obtained in which the capacity of the 500<sup>th</sup> cycle was 83% of the initial capacity.

#### EXAMPLE 2-2

An electrolytic solution was prepared by substantially the same manner as that of Example 1-2, in which  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  was replaced with  $\text{LiPF}_6$ . The resulting electrolytic solution had a lithium borate derivative concentration of 0.10 mol/liter and a  $\text{LiPF}_6$  concentration of 0.90 mol/liter.

The test cell was prepared in the same manner as that of Example 2-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 2-1. The capacity of the 500<sup>th</sup> cycle was 84% of the initial capacity.

#### EXAMPLE 2-3

An electrolytic solution was prepared by substantially the same manner as that of Example 1-3, in which  $\text{LiN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$  was replaced with  $\text{LiBF}_4$ . The resulting electrolytic solution had a lithium borate derivative concentration

of 0.05 mol/liter and a  $\text{LiBF}_4$  concentration of 0.95 mol/liter.

The test cell was prepared in the same manner as that of Example 2-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 2-1.

- 5 The capacity of the 500<sup>th</sup> cycle was 79% of the initial capacity.

#### EXAMPLE 2-4

A solution was prepared by adding acetonitrile to 80 parts by weight of a polyethylene oxide (average molecular weight: 10,000). Then, 10 parts by weight of a lithium borate derivative,  
10 represented by the same formula as that of Example 1-1, and 10 parts by weight of  $\text{LiPF}_6$  were added to the solution. The resulting mixture was cast on a glass, followed by drying to remove the acetonitrile. With this, a polymer solid electrolyte film was prepared.

- 15 The test cell was prepared in the same manner as that of Example 2-1 except in that the polymer solid electrolyte film was used in place of the electrolytic solution and the separator. In fact,  $\text{LiCoO}_2$  was used as a positive electrode material, and natural graphite was used as a negative electrode material. A constant  
20 current charging and discharging test was conducted at 70°C under the following conditions. The current density was 0.1  $\text{mA}/\text{cm}^2$  for both charging and discharging, while charging was performed until 4.2 V and discharging until 3.0 V (vs.  $\text{Li}/\text{Li}^+$ ). As  
25 a result, the initial discharge capacity was 120  $\text{mAh/g}$  (the positive electrode capacity). Although charging and discharging were repeated 500 times, results were obtained in which the capacity of the 500<sup>th</sup> cycle was 85% of the initial capacity.

#### COMPARATIVE EXAMPLE 2-1

- At first,  $\text{LiPF}_6$  was dissolved in a mixture of ethylene  
30 carbonate (EC) and dimethyl carbonate (DMC) ( $\text{EC}:\text{DMC} = 1:1$  by volume) to prepare an electrolytic solution having a  $\text{LiPF}_6$  concentration of 1.0 mol/liter.

The test cell was prepared in the same manner as that of

Example 2-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 2-1. The capacity of the 500<sup>th</sup> cycle was 64% of the initial capacity.

#### COMPARATIVE EXAMPLE 2-2

5        At first,  $\text{LiBF}_4$  was dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a  $\text{LiBF}_4$  concentration of 1.0 mol/liter.

10       The test cell was prepared in the same manner as that of Example 2-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 2-1. The capacity of the 500<sup>th</sup> cycle was 46% of the initial capacity.

#### EXAMPLE 3-1

15       A lithium borate derivative, represented by the same formula as that of Example 1-1, and  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  were dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC = 1:1 by volume) to prepare an electrolytic solution having a lithium borate derivative concentration of 0.01 mol/liter and a  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  concentration of 0.99  
20       mol/liter.

      A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li/Li}^+$ ), there was no flow of current whatsoever. Following testing, although the surface of the  
25       working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

      The test cell was prepared by the same manner as that of Example 2-1. A constant current charging and discharging test was conducted by the same manner as that of Example 2-1, except  
30       that the test was conducted at an environmental temperature of 25°C. The capacity of the 500<sup>th</sup> cycle was 83% of the initial capacity.

#### EXAMPLE 3-2

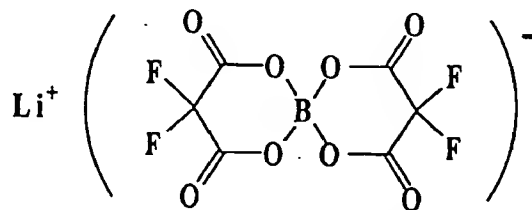
A lithium borate derivative, represented by the same formula as that of Example 1-1, and  $(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{NLi}$  were dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC = 1:1 by volume) to prepare an electrolytic solution  
5 having a lithium borate derivative concentration of 0.80 mol/liter and a  $(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{NLi}$  concentration of 0.10 mol/liter.

A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li/Li}^+$ ), there was no flow of current  
10 whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

The test cell was prepared by the same manner as that of Example 2-1. A constant current charging and discharging test  
15 was conducted by the same manner as that of Example 2-1, except that the test was conducted at an environmental temperature of 60°C. The capacity of the 500<sup>th</sup> cycle was 78% of the initial capacity.

### EXAMPLE 3-3

A lithium borate derivative, represented by the following formula, and  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  were dissolved in a mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (EC:EMC = 1:1 by volume) to prepare an electrolytic solution  
20 having a lithium borate derivative concentration of 0.70 mol/liter and a  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  concentration of 0.30 mol/liter.  
25



A corrosion test of an aluminum collector was performed in the same manner as that of Example 1-1. When the working electrode was held at 5 V ( $\text{Li/Li}^+$ ), there was no flow of current

whatsoever. Following testing, although the surface of the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

5 The test cell was prepared by the same manner as that of Example 2-1. A constant current charging and discharging test was conducted by the same manner as that of Example 2-1, except that the test was conducted at an environmental temperature of 60°C. The capacity of the 500<sup>th</sup> cycle was 81% of the initial capacity.

10 EXAMPLE 3-4

A solution was prepared by adding acetonitrile to 70 parts by weight of a polyethylene oxide (average molecular weight: 10,000). Then, 5 parts by weight of a lithium borate derivative, represented by the same formula as that of Example 1-1, and 25 parts by  
15 weight of  $((CF_3)_2CHOSO_2)_2NLi$  were added to the solution. The resulting mixture was cast on a glass, followed by drying to remove the acetonitrile. With this, a polymer solid electrolyte film was prepared.

A corrosion test of an aluminum collector was performed  
20 using a laminate including the solid electrolyte film interposed between an aluminum electrode (working electrode) and a lithium electrode. This laminate was prepared by press welding. When the working electrode was held at 5 V (Li/Li<sup>+</sup>), there was no flow of current whatsoever. Following testing, although the surface of  
25 the working electrode was observed by SEM, there were no changes observed in comparison with that before testing.

The test cell was prepared by using the polymer solid electrolyte film in place of the electrolytic solution and the separator. Furthermore, LiCoO<sub>2</sub> and lithium metal foil were  
30 respectively used for the positive and negative electrodes. A constant current charging and discharging test was conducted in the same manner as that of Example 2-4 except that charging and discharging were repeated 100 times. As a result, the initial



discharge capacity was 120 mAh/g (the positive electrode capacity).  
The capacity of the 100<sup>th</sup> cycle was 88% of the initial capacity.

#### COMPARATIVE EXAMPLE 3-1

At first,  $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  was dissolved in a mixture of  
5 ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC:DMC  
= 1:1 by volume) to prepare an electrolytic solution having a  
 $((\text{CF}_3)_2\text{CHOSO}_2)_2\text{NLi}$  concentration of 1.0 mol/liter.

A corrosion test of an aluminum collector was performed in  
the same manner as that of Example 1-1. When the working  
10 electrode was held at 5 V (Li/Li<sup>+</sup>), corrosion current was observed.  
Following testing, the surface of the working electrode was  
observed by SEM. With this, many pits were observed on its  
surface. It is assumed that these pits were caused by corrosion.

The test cell was prepared in the same manner as that of  
15 Example 2-1, and a constant current charging and discharging  
test was conducted in the same manner as that of Example 2-1,  
except that the test was conducted at an environmental  
temperature of 25°C. The capacity of the 500<sup>th</sup> cycle was 62% of  
the initial capacity.

#### COMPARATIVE EXAMPLE 3-2

At first,  $(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{NLi}$  was dissolved in a mixture of  
ethylene carbonate (EC) and diethyl carbonate (DEC) (EC:DEC =  
1:1 by volume) to prepare an electrolytic solution having a  
 $(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{NLi}$  concentration of 1.0 mol/liter.

A corrosion test of an aluminum collector was performed in  
the same manner as that of Example 1-1. When the working  
25 electrode was held at 5 V (Li/Li<sup>+</sup>), corrosion current was observed.  
Following testing, the surface of the working electrode was  
observed by SEM. With this, many pits were observed on its  
30 surface. It is assumed that these pits were caused by corrosion.

The test cell was prepared in the same manner as that of  
Example 2-1, and a constant current charging and discharging  
test was conducted in the same manner as that of Example 2-1,

except that the test was conducted at an environmental temperature of 60°C. The capacity of the 500<sup>th</sup> cycle was 58% of the initial capacity.

### COMPARATIVE EXAMPLE 3-3

5       At first, a lithium borate derivative, represented by the same formula as that of Example 1-1, was dissolved in a mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) (EC:EMC = 1:1 by volume) to prepare an electrolytic solution having a lithium borate derivative concentration of 0.8 mol/liter.

10       The test cell was prepared in the same manner as that of Example 2-1, and a constant current charging and discharging test was conducted in the same manner as that of Example 2-1, except that the test was conducted at an environmental temperature of 60°C. The capacity of the 500<sup>th</sup> cycle was 64% of  
15       the initial capacity.

20       The entire disclosure of Japanese Patent Applications No. 2000-360540 and 2000-360541 each filed on November 28, 2000, and No. 2001-257159 filed on August 28, 2001, including specification, claims and summary, is incorporated herein by reference in its entirety.

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